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First *P*-Trifluoromethylated Ylides

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ABSTRACT

Trifluoromethylated phosphines R_2PCF_3 (R = NEt_2, Me, ${}^{i}Pr$) were methylated by $CH_3OSO_2CF_3$, yielding the corresponding phosphonium salts $[R_2P(CF_3)CH_3]^+$ $[F_3CSO_3]^-$. Treatment with $LiN(SiMe_3)_2$ at −80°C furnished the phosphorus ylides $R_2P(CF_3){=}CH_2$ that could be trapped by use of hexafluoroacetone with formation of stable $1,2\lambda^5\sigma^5$-oxaphosphetanes. The single-crystal X-ray structure determination of one of these oxaphosphetanes showed a distorted trigonal bipyramid at phosphorus with the P–CF_3 group in an axial position.

INTRODUCTION

Phosphorus ylides containing fluorine or perfluoroalkyl groups in the alkylidene moiety [1] and P-halogeno ylides [2,3] are versatile reactants in organic chemistry. *P*-perfluoroalkylated methylene phosphoranes, however, have not been synthesized and trapped up to the present time, to the best of our knowledge. The strong electron-withdrawing effect on phosphorus without π backbonding should influence the ylide reactivity [4]. Deprotonation of the phosphonium salts $[(H_3C)_3PC_6F_{13}]^+$ X^- and $[(H_3C)_2P(C_6F_{13})_2]^+$ X^- using KH or ^{n}BuLi resulted in the oligomerization of the respective methylene phosphoranes [4]. Since trifluoromethylated phosphines, e.g., R_2PCF_3 (R = $N(C_2H_5)_2$ [5], CH_3 [6]) are accessible using "RUPPERT's reagent" [5], (CF_3Br/$P[N(C_2H_5)_2]_3$), methylation followed by deprotonation at low temperatures should yield the expected *P*-trifluoromethylated ylides that could be trapped by hexafluoroacetone, for example.

RESULTS AND DISCUSSION

The trifluoromethylphosphines R_2PCF_3, **1a–c** (a: R = $N(C_2H_5)_2$, b: R = CH_3, c: R = $CH(CH_3)_2$) were methylated using methyl triflate at room temperature giving the respective phosphonium salts $[R_2P(CH_3)CF_3]^+$ $[CF_3SO_3]^-$, **2a–c** (Scheme 1), colorless solids, which were deprotonated by lithium bis(trimethylsilyl)amide at −80°C in THF to form yellow solutions of the ylides $R_2P(CF_3){=}CH_2$ **3a–c** (Scheme 1).

In the case of **3a** (R = $N(C_2H_5)_2$) and **3c** (R = $CH(CH_3)_2$), the solutions were stable for more than 2 months at 25°C. Above this temperature, the solutions turned brown, and black solids precipitated that were not investigated, yet. The ylides **3a–c** could be trapped by [2 + 2] cycloaddition to hexafluoroacetone to give the $1,2\lambda^5\sigma^5$-oxaphosphetanes **4a–c** (Scheme 1). Compounds **4a** and **4c** are moisture-sensitive, colorless liquids, but **4b** is a solid.

The single-crystal X-ray structure determination of **4b** (Figure 1) exhibits a distorted trigonal-bipyr-

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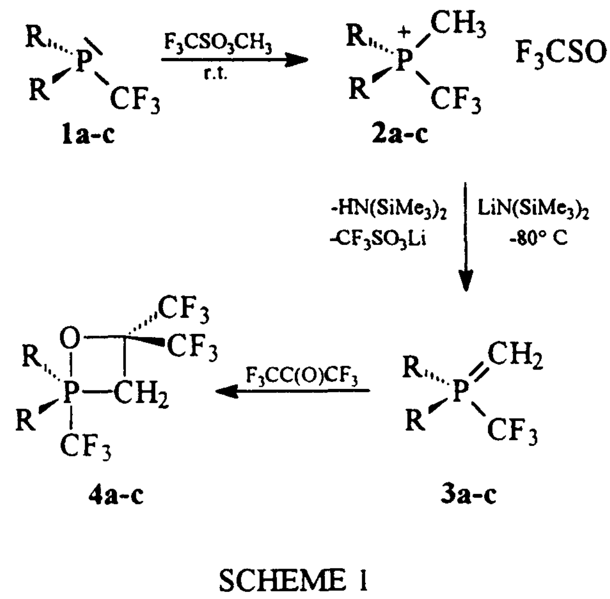

SCHEME 1

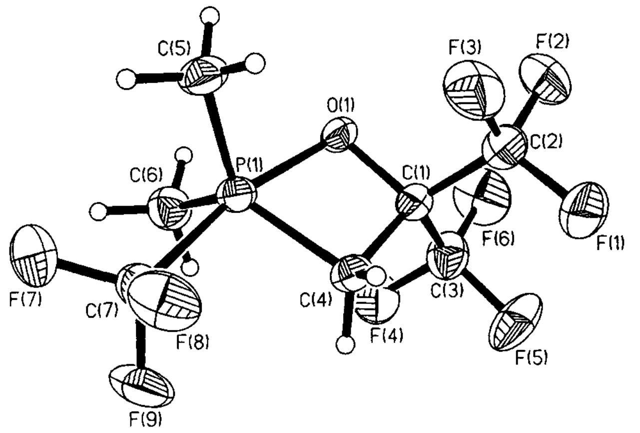

FIGURE 1 X-ray structure determination of **4b** (thermal ellipsoids at 50% probability).

amidal geometry at phosphorus with an O(1)–P(1)–C(7) angle of 167.57(14)°. The CF_3 group occupies an apical position, and the planar oxaphosphetane ring spans an axial-equatorial position with a dihedral angle C(4)–P(1)–O(1)–C(1) of 0.4°. Similar parameters had been found in comparable oxaphosphetanes [7,8]; as expected, the $P(1)–C(7)F_3$ bond length (191.5(4) pm) was found to be considerably longer than those of the nonfluorinated equatorial methyl groups at phosphorus with 179.5(3) and 178.6(3) pm, respectively.

TABLE 1 X-ray Structure Determination of **4b**. Selected Bond Lengths [pm] and Bond Angles [°].

P(1)–O(1)	183.7(2)	P(1)–C(7)	191.5(4)
P(1)–C(5)	179.5(3)	P(1)–C(6)	178.6(3)
P(1)–C(4)	183.1(3)	C(4)–C(1)	152.3(4)
C(1)–O(1)	140.4(3)	C(1)–C(2)	152.0(5)
C(1)–C(3)	53.0(4)		
O(1)–P(1)–C(7)	167.6(2)	O(1)–P(1)–C(4)	75.0(1)
P(1)–C(4)–C(1)	90.9(2)	C(4)–C(1)–O(1)	99.4(2)
C(1)–O(1)–P(1)	94.7(2)	C(5)–P(1)–C(6)	114.8(2)
C(5)–P(1)–C(4)	120.7	C(6)–P(1)–C(4)	123.3(2)

The proposed structures of the new compounds were confirmed by their NMR spectroscopic data (Table 1). The ^{31}P shift values are located in the expected range [9], and characteristic ^1H resonances for the $H_2C=P$ moiety were observed for **3a** (δ_H = 0.49, $^2J_{PH}$ = 14.1 Hz) and **3c** (δ_H = 0.23, $^2J_{PH}$ = 18.1 Hz) [10]. The $^2J_{PF}$ values of **4c** (0.8 Hz) and of **4b** (21.5 Hz) are characteristic for an apical bonded CF_3 group in a trigonal bipyramid at phosphorus [6,11]. The methyl groups in the $(CH_3)_2CH$ moieties for compounds **1c**, **2c**, and **4c** are diastereotopic and magnetically nonequivalent (see Experimental).

EXPERIMENTAL

The appropriate precautions in handling moisture-sensitive compounds were observed throughout this work. Elemental analyses were undertaken by Mikroanalytisches Laboratorium Beller, Göttingen, Germany. Mass spectra (EI, 70 eV) were carried out on a Finnigan MAT 8200 instrument. NMR spectra were obtained on a Bruker AC 80 instrument operating at 80.13 MHz (^1H, internal standard TMS), at 75.39 MHz (^{19}F, internal standard CCl_3F) and at 32.44 MHz (^{31}P, external standard 85% H_3PO_4).

The X-ray structural study of compound **4b** (crystallized from pentane, crystal size 0.50 × 0.40 × 0.40 mm³, orthorhombic Pbca with a = 877.90(10), b = 1306.60(10), c = 1965.3(2) pm, Z = 8, D = 1.827 Mg/m³) was performed at 173 K on a Siemens P4 diffractometer using graphite monochromated Mo-$K\alpha$ radiation (λ = 71.073 pm), θ range 2.98–25.01°, reflections measured 4919, unique reflections 1983 (R_{int} = 0.0561). The structure was solved by direct methods and refined by full-matrix least-squares using SHELXTL PLUS (VMS); goodness of fit at F^2 0.743, final R values (1045 reflections) [$I > 2\sigma(I)$] for 1045; R1 = 0.0387, wR2 = 0.0723; R value (1983 reflections) R1 = 0.0903, wR2 = 0.0808.

Diisopropyltrifluoromethylphosphine (**1c**). To a solution of 100 mmol $[(H_3C)_2CH]_2PCl$ and 120 mmol CF_3Br in 120 mL triglyme were added 100 mmol $P[N(C_2H_5)_2]_3$ at −70°C. Distillation yielded 55 mmol **1c** (55%, bp 142°C). NMR: ^1H: δ = 1.01 (Me_2CH, 6 H, dd, $^3J_{HH}$ = 7.0, $^3J_{HP}$ = 7.0 Hz), 1.08 (Me_2CH, 6 H, dd,

$^3J_{HH}$ = 7.0, $^3J_{HP}$ = 7.0 Hz), 1.7–2.1 (*Me*$_2$C*H*, 2 H, *m*); ^{19}F: δ = −51.1 (F$_3$C–P, d, $^2J_{PF}$ = 52.2 Hz); ^{31}P: δ = 23.7 (q). MS (200°C): *m*/*e* (%) = 186 (M$^+$, 36), 158 (M$^+$ −C$_2$H$_4$, 5), 144 (M$^+$ −C$_3$H$_6$, 18), 117 (M$^+$ −CF$_3$, 8), 75 (M$^+$ −C$_3$H$_6$, −CF$_3$, 7), 69 (CF$_3^+$, 8), 65 (10), 43 (C$_3$H$_7^+$, 100) and other fragments. Anal calcd for C$_7$H$_{14}$F$_3$P (186.08): C, 45.14; H, 7.66; F, 30.60; P, 15.36. Found: C, 44.75; H, 7.58; F, 28.70; P, 16.65.

TABLE 2 ^{19}F and ^{31}P NMR Data of Compounds **3a–c** and **4a–c** (*J* in Hz)

Compound	$\delta_F(CF_3P)^a$	$\delta_F(CF_3C)^a$	$\delta_P{}^a$ ($^2J_{PF}$)
3a[b]	−72.5	—	52.1 (82.7)
3b	−76.0	—	10.7 (62.0)
3c[c]	−64.2	—	41.5 (46.0)
4a[d]	−59.3	−75.5	−39.5 (44.3)
4b[e]	−75.2	−78.2	−79.0 (21.5)
4c[f]	−59.6	−76.2	−54.3 (0.8)

[a] Hihg-field shifts from CCl$_3$F and 85% H$_3$PO$_4$ were given negative signs.

[b] ^{1}H: δ = 0.49 (=CH$_2$, 2 H, d, $^2J_{PH}$ = 14.1), 1.04 (C*H*$_3$CH$_2$, 12 H, t, $^3J_{HH}$ = 7.0), 3.09 (CH$_3$C*H*$_2$, 8 H, dq, $^3J_{PH}$ = 10.7).

[c] ^{1}H: δ = 0.23 (=CH$_2$, 2 H, d, $^2J_{HP}$ = 18.1), 0.91 (*Me*$_2$CH, 6 H, d, $^3J_{HH}$ = 7.0), 1.13 (*Me*$_2$CH, 6 H, d, $^3J_{HH}$ = 7.0), 3.1–3.7 (Me$_2$C*H*, 2 H, m).

[d] ^{1}H: δ = 0.94 (C*H*$_3$CH$_2$, 12 H, t, $^3J_{HH}$ = 7.1), 3.00 (CH$_3$C*H*$_2$, 8 H, dq, $^3J_{HP}$ = 13.1), 3.87 (PCH$_2$, d, $^2J_{HP}$ = 15.8).

[e] ^{1}H: δ = 1.27 (PCH$_3$, d, $^2J_{HP}$ = 15.0), 3.61 (PCH$_2$, $^2J_{HP}$ = 17.4).

[f] ^{1}H: δ = 1.01 (*Me*$_2$CH, 6 H, dd, $^3J_{HH}$ = 6.9, $^3J_{HP}$ = 6.9), 1.27 (*Me*$_2$CH, 6 H, dd, $^3J_{HH}$ = 6.9, $^3J_{HP}$ = 6.9), 1.9–2.6 (Me$_2$C*H*, 2 H, m), 3.84 (PC*H*$_2$, $^2J_{HP}$ = 17.2).

Bis(diethylamino)methyltrifluoromethylphosphonium (**2a**) *and Diisopropylmethyltrifluoromethylphosphonium Triflate* (**2c**). To a solution of 21.5 mmol **1a** (**1c**) in 25 mL CH$_2$Cl$_2$ were added 21.5 mmol F$_3$CSO$_3$CH$_3$ at room temperature. The solution was stirred for 2 hours. Removal of the solvent yielded 18.3 mmol **2a** (85%, mp 95°C) and 17.2 mmol **2c** (80%, mp 143°C), respectively. **2a**: NMR: ^{1}H: δ = 1.25 (C*H*$_3$CH$_2$, 12 H, t, $^3J_{HH}$ = 7.1 Hz), 2.37 (CH$_3$-P, 3 H, d, $^2J_{PH}$ = 14.0 Hz), 3.32 (CH$_3$C*H*$_2$, 8 H, dq, $^3J_{PH}$ = 12.3 Hz); ^{19}F: δ = −61.4 (F$_3$C–P, d, $^2J_{PF}$ = 101 Hz). −74.5 (F$_3$C–S, s); ^{31}P: δ = 47.5 (q). Anal calcd for C$_{11}$H$_{23}$F$_6$N$_2$O$_3$PS (408.11): C, 32.34; H, 5.68; F, 27.93; P, 7.59. Found: C, 32.05; H, 5.63; F, 27.70; P, 7.59. **2c**: NMR: ^{1}H: δ = 1.36 (*Me*$_2$CH, 6H, $^3J_{HH}$ = 7.2 Hz), 1.60 (*Me*$_2$CH, 6H, $^3J_{HH}$ = 7.2 Hz), 2.24 (CH$_3$–P, d, $^2J_{HP}$ = 7.2 Hz), 2.8–3.5 (Me$_2$C*H*, 2 H, m); ^{19}F: δ = −52.6 (F$_3$C–P, d, $^2J_{PF}$ = 74.3 Hz), −74.5 (F$_3$C–S, s); ^{31}P: δ = 64.0 (q). Anal calcd for C$_9$H$_{17}$F$_6$O$_3$PS (350.05): C, 30.85; H, 4.89; F, 32.6; P, 8.85. Found: C, 30.86; H, 5.01; F, 32.2; P, 8.80.

General Procedure for the Formation of Compounds **3a–c** *and* **4a–c**. To a solution of 10 mmol **2a–c** in 10 mL THF were added 10 mmol lithium bis(trimethylsilyl)amide in 8 mL hexane at −80°C. After having been stirred for 1 hour, the solution turned yellow and was characterized by NMR spectroscopy at this temperature (Table 2). Hexafluoroacetone (15 mmol) was added to the solution, was allowed to warm to room temperature over a period of 12 hours. All volatile products were removed in vacuo, and the residue was extracted with pentane. In the case of **4a** and **4b**, after removal of pentane, the remaining pale yellow oils were distilled in vacuo; **4c** was crystallized from pentane solution.

2,2-Bis(diethylamino)-2,4,4-tris(trifluoromethyl)-1,2λ^5-oxaphosphetane (**4a**). Bp (0.001 mbar) 56°C (yield 51%). MS (30°C): *m*/*e*(%) = 405 (M$^+$ −F, 3), 355 (M$^+$ −CF$_3$, 76), 352 (M$^+$ −(C$_2$H$_5$)$_2$N, 100), 302 (M$^+$ −122, 22), 284 (HPN(C$_2$H$_5$)$_2$ CH$_2$C(CF$_3$)$_2$O$^+$, 22), 191 ((C$_2$H$_5$)$_2$NP(F)CF$_3^+$, 17), 138 ((C$_2$H$_5$)$_2$NP(O)F$^+$, 24), 122 ((C$_2$H$_5$)$_2$N=PF$^+$, 14), 72 ((C$_2$H$_5$)$_2$N$^+$, 47), 29 (C$_2$H$_5^+$, 13), and other fragments. Anal calcd for C$_{13}$H$_{22}$F$_9$N$_2$OP (424.13) : C, 36.78; H, 5.23; F, 40.30; P, 7.30. Found: C, 36.34; H, 5.47; F, 38.80; P, 7.02.

2,2-Dimethyl-2,4,4-tris(trifluoromethyl)-1,2λ^5-oxaphosphetane (**4b**). Mp 68°C (yield 15%). MS (200°C): *m*/*z* (%): 310 (M$^+$, <1), 231 (M$^+$ − F, 7), 241 (M$^+$ − CF$_3$, 100), 191 (M$^+$ − C$_2$F$_5$, 13), 171 (M$^+$ − C$_2$F$_5$ − HF, 3), 144 ((CH$_3$)$_2$P(CF$_3$)CH$_2^+$, 6), 77 ((CH$_3$)$_2$PO$^+$, 18), 75 ((CH$_3$)$_2$PCH$_2^+$, 16), 69 (CF$_3^+$, 2), and other fragments. Precision mass determination for *m*/*z* = 241: 241.02197 (found), 241.02170 (calcd) (for C$_6$H$_8$OF$_6$P) (−1.1 ppm, −0.3 mmu).

2,2-Diisopropyl-2,4,4-tris(trifluoromethyl)-1,2λ^5-oxaphosphetane (**4c**). Bp (0.001 mbar) 31°C (yield 32%). MS (20°C): *m*/*e* (%) = 366 (M$^+$, 5), 347 (M$^+$ −F, 4), 323 (M$^+$ −C$_3$H$_7$, 15), 297 (M$^+$ −CF$_3$, 54), 255 (M$^+$ −CF$_3$ −C$_3$H$_6$, 9), 147 (3), 105 ((C$_3$H$_7$)$_2$P(O)CH$_2^+$, 2), 73 (5), 43 (C$_3$H$_7^+$, 100), 27 (C$_2$H$_3^+$, 6), and other fragments. Anal calcd for C$_{11}$H$_{16}$F$_9$OP (366.08): C, 36.06; H, 4.40; F, 46.70; P, 8.46. Found: C, 35.60; H, 4.18; F, 45.50; P, 8.35.

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